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A STUDY OF POLYMERS  
CONTAINING SILICON-NITROGEN BONDS

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Progress Report 31 for the Period  
August 4, 1963 to September 3, 1963

To

GEORGE C. MARSHALL SPACE FLIGHT CENTER  
National Aeronautics and Space Administration  
Huntsville, Alabama

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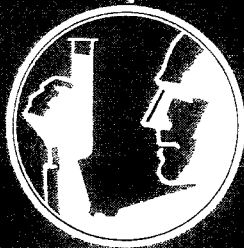
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Project 1259, Report 31

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## ABSTRACT

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Polymerization mechanisms of N-trimethylsilylhexaphenylcyclotrisilazane and hexaphenylcyclotrisilazane were compared. N-trimethylsilylhexaphenylcyclotrisilazane was found to evolve at least 18 different compounds as it was polymerized by heat. Benzene was 80% of the evolved material, and the rest included compounds boiling both above and below benzene. Hexaphenylcyclotrisilazane evolved almost exclusively benzene on polymerization. The trimethylsilyl group of N-trimethylsilylhexaphenylcyclotrisilazane evidently took part in the polymerization.

In an effort to prepare fluid unsymmetrical silazanes for lubricants, an impure compound believed to consist of N-methyl derivatives of hexaphenylcyclotrisilazane was prepared but not completely purified and characterized. The N-methyl groups apparently stabilized the entire molecule toward hydrolysis and reduced the melting point, but not as far as desired.

Several polymers with phenylene rings separating -Si-N-Si- groups were prepared. All were capable of further polymerization to materials with good thermal stability, but no high polymers were made.

A mixture of silazanes that was liquid at room temperature and boiled at about 400°C was prepared by treating methylphenyldichlorosilane with methylamine and ammonia. It, or related materials, could have merit as hydraulic fluids. Polymerization of the mixture is being studied further.

AUTHOR

## A STUDY OF POLYMERS CONTAINING SILICON-NITROGEN BONDS

### I. PURPOSE AND STATUS OF THE PROJECT

Silicon-nitrogen compounds are being studied in an effort to produce thermally stable materials that will be useful in the space program. This report covers the fifth month of the fourth year of the program.

The use of the N-alkali derivatives of cyclic silazanes has proven to be of less value than we hoped because of the difficulty of obtaining pure simple compounds or polymers with high molecular weights. However, the potential value of finding a good synthesis method based on the N-alkali silazanes justifies carrying the study on as originally planned.

N-Carbonyl derivatives of silazanes appear to be unstable, and no promising compounds or polymers have been made in spite of considerable effort. Further work on them is not recommended.

The silicon-nitrogen polymers with phenylene bridges between -Si-N-Si- units are promising because of their excellent thermal stability. They are difficult to make, and, so far, no high polymers have been made; but the work is being continued.

In the coming month, we expect to complete the planned investigation of about half of the subjects on the year's agenda, and work on several new subjects will be started.

## II. POTASSIUM DERIVATIVES OF SILAZANES AS INTERMEDIATES FOR SYNTHESIS

### A. Discussion

The N-alkali derivatives of silylamines react with compounds having active halogens, thereby offering a method of preparing a variety of substituted silylamines.



The reaction has been studied extensively in other laboratories, and we are presently using it in attempts to make polymers and liquids of exceptional thermal stability. It now appears that the reaction is subject to disproportionation, which makes it difficult to obtain pure products except by extensive fractional crystallization.

In previous reports, the attachment of benzyl and trimethylsilyl groups to silazanes has been shown to increase their hydrolytic stability. The resulting compounds were polymerized by heating, but no polymers of high molecular weight were obtained. In the past month, we studied the polymerization reaction in more detail in the hope that a better understanding of it would lead to a method of getting higher molecular weights and, consequently, better strength.

Attempts to prepare acetyl derivatives of hexaphenylcyclotrisilazane by way of the N-alkali derivative have been unsuccessful. The products were sticky polymers, and no promising reactions were found.

1. Studies of the polymerization of N-trimethylsilylhexaphenylcyclotrisilazane

N-trimethylsilylhexaphenylcyclotrisilazane condensed on heating above 450°C to form, first, a high-melting benzene-soluble polymer and, then, an infusible and insoluble polymer.

It was evident from the data obtained that the mechanism of polymerization had much in common with that of the polymerization of hexaphenylcyclotrisilazane and proceeds by the elimination of benzene through the interaction of  $\equiv\text{Si-Ph}$  and  $\text{H-N}\equiv$  groups in adjacent molecules.

The polymerization was done in a glass vessel over a gas burner, and samples were taken periodically for analysis. The polymerization was also done in a distilling apparatus, and the volatile products were trapped for analysis. The results did not permit any simple interpretation of the mechanism. The samples that were taken periodically during polymerization indicated that a steady state was reached at approximately the composition  $\text{C}_{6.5}\text{H}_{5.5}\text{N}_{0.5}\text{Si}_{1.0}$ . The data are listed in Table I and plotted graphically in Figure 1. However, the data cannot be considered conclusive, because the analyses failed to add up to 100%, and it does not appear likely that the missing amounts can be attributed entirely to oxygen. The similarity of Figure 1 to a comparable curve drawn for hexaphenylcyclotrisilazane<sup>1</sup> is striking. Condensation occurred rapidly while the mass was being heated from 480-560°C, and then it changed only a little during another 50 minutes of heating at 550°C.

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1. Annual Summary Report, Contract NAS 8-1510, George C. Marshall Space Flight Center, February 28, 1962, page 91.

**Table I. Characteristics of Precursors of the N-trimethylsilylhexaphenylcyclotrisilazane Polymer**

	Starting material		I		II		III		IV		V	
	Compo- sition, %	Combining ratio <sup>a</sup>	Compo- sition, %	Combining ratio <sup>a</sup>	Compo- sition, %	Combining ratio <sup>a</sup>	Compo- sition, %	Combining ratio <sup>a</sup>	Compo- sition, %	Combining ratio <sup>a</sup>	Compo- sition, %	Combining ratio <sup>a</sup>
Time of heating, min	0		6		10		12		15		65	
Temperature when sample taken, °C	-		481		540		558				550	
Approximate melting point of sample, °C	168-170		61-70		128-142		above 350		infusible		infusible	
Physical state, when cool	crystalline		vitreous		vitreous		vitreous		foamed, vitreous		foamed, vitreous	
Solubility in benzene	soluble		soluble		soluble		slightly soluble		insoluble		insoluble	
	Starting material		I		II		III		IV		V	
	Compo- sition, %	Combining ratio <sup>a</sup>	Compo- sition, %	Combining ratio <sup>a</sup>	Compo- sition, %	Combining ratio <sup>a</sup>	Compo- sition, %	Combining ratio <sup>a</sup>	Compo- sition, %	Combining ratio <sup>a</sup>	Compo- sition, %	Combining ratio <sup>a</sup>
Carbon	70.87	5.90	69.54	5.77	69.06	5.74	65.69	5.46	62.85	5.24	57.79	4.81
Hydrogen	5.97	5.93	5.54	5.50	5.62	5.58	4.50	4.46	4.67	4.64	4.17	4.14
Nitrogen	6.65	0.48	6.51	0.46	7.10	0.51	6.27	0.44	4.06	0.29	5.56	0.39
Silicon	16.6	0.59	18.41 <sup>b</sup>	0.65	17.5	0.62	19.6	0.69	21.1	0.75	21.3	0.76
	100.09				99.28		96.06		92.68		88.82	

Ratios to Si ■ 4: Theoretical formula,  $C_{39}H_{41}N_3Si_4$ 

Carbon	40.0	35.5	37.0	31.7	28.0	25.3
Hydrogen	40.2	33.8	36.0	25.9	24.8	21.8
Nitrogen	3.26	2.83	3.29	2.55	1.55	2.05

<sup>a</sup> Combining ratio =  $\frac{\text{composition}}{\text{atomic weight}}$

b Too little sample for silicon analysis, silicon by difference.

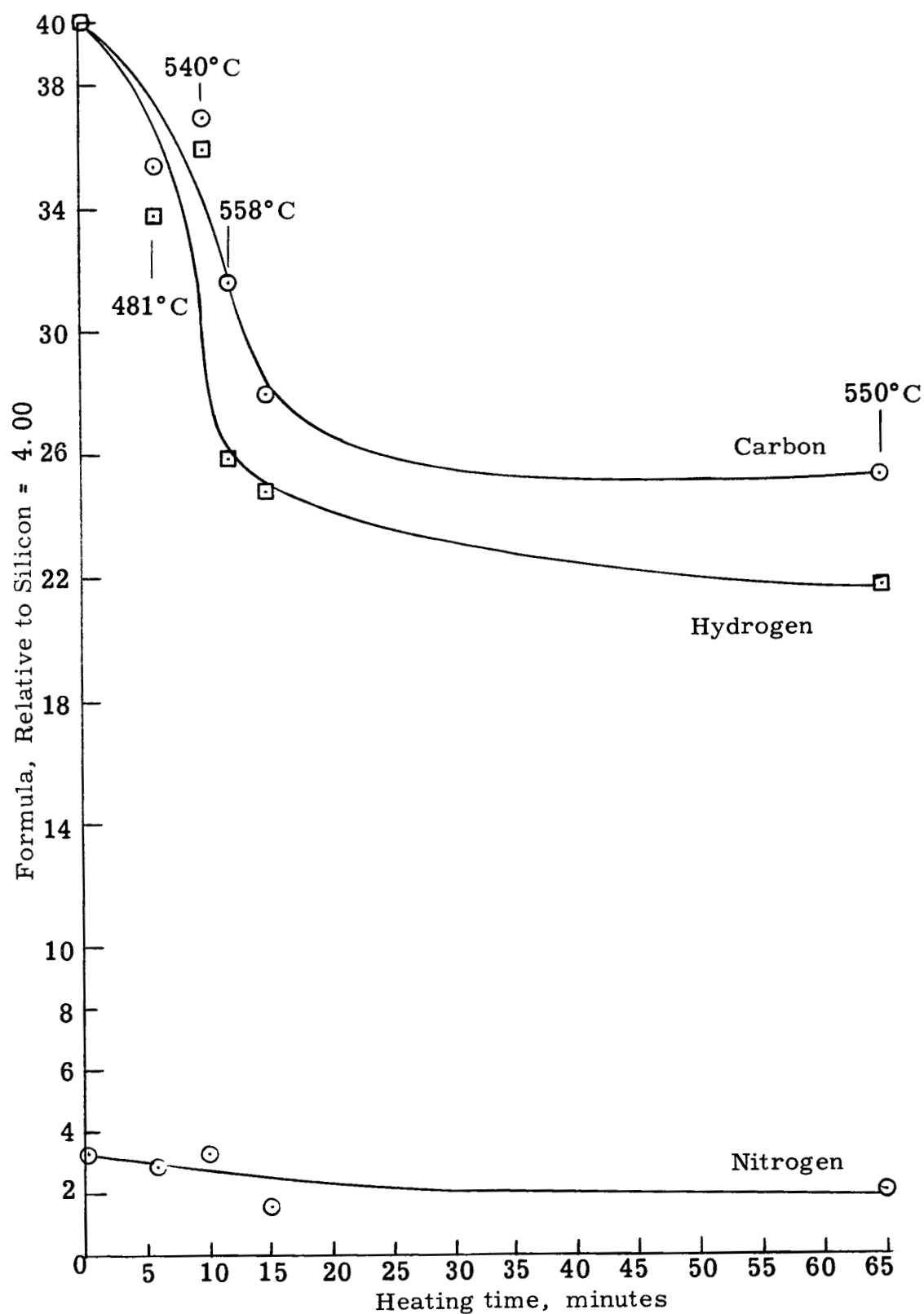


Figure 1. Change in Composition During Thermal Polymerization of N-Trimethylsilylhexaphenylcyclotrisilazane (See Table I)



The volatile products of the condensation polymerization were 80% benzene, as shown by gas chromatography. About 10% consisted of four compounds boiling lower than benzene, including hydrogen and methane, and the other 10% consisted of 13 compounds boiling higher than benzene. Toluene, xylene, and biphenyl were believed to be present in the condensate, but they were not completely identified.

It is clear that the polymerization of N-trimethylsilylhexaphenylcyclotrisilazane is more complicated than that of hexaphenylcyclotrisilazane. There seems little merit in carrying the identification of products further. The most important question is whether a useful polymer can be made by thermal polymerization, and it is evident that the trimethylsilyl group has not decreased the functionality of the molecule significantly. So far, the polymers have been excessively brittle, but they do have high softening points and high thermal stability, and they are soluble in benzene. Higher molecular weight is needed.

## 2. Attempts to prepare N-alkyl derivatives of hexaphenylcyclotrisilazane

Hexaphenylcyclotrisilazane has been alkylated by treating N-potassium derivatives of hexaphenylcyclotrisilazane with methyl iodide and n-butyl iodide. The object is to produce cyclic silazanes that are useful as lubricants, compounds that remain liquid over wide temperature ranges, or raw materials that can be converted to useful polymers. A pure N-methyl derivative was not isolated, but the mixture was more stable to acid hydrolysis than hexaphenylcyclotrisilazane. Attempts are now being made to polymerize the N-methyl derivatives. The substitution of methyl for hydrogen is expected to reduce the functionality and to increase the proportion of linear polymerization as contrasted to cross-linking. We will attempt to prepare N-alkyl derivatives of cyclic silazanes with longer side chains to increase the chances of their being liquids.

## B. Experimental Details

### 1. Studies of the polymerization of N-trimethylsilylhexaphenylcyclotrisilazane

#### a. Samples taken periodically during polymerization

The procedure was taken from previous work on the polymerization of hexaphenylcyclotrisilazane.<sup>1</sup>

N-trimethylsilylhexaphenylcyclotrisilazane, 3 g, was placed in a test tube. A 600°C thermometer was placed loosely in the test tube, and the apparatus was flushed with nitrogen. The test tube was heated gently with a gas flame, and the crystals melted at about 170°C. Continued heating produced a few bubbles, but the liquid did not appear to boil until the temperature reached 451°C. Boiling continued while the melt temperature rose to 481°C in 6 minutes. At this time, heating was discontinued while Sample I was removed with a small stainless steel scoop. Heating was resumed, and after boiling for 4 additional minutes while the temperature rose to 540°C, Sample II was taken. After 2 additional minutes Sample III was taken at 558°C. As the scoop was withdrawn, brittle fibers formed. Solid began to appear in the tube shortly after Sample III was taken; and thereafter the temperature measurement was erratic because of poor contact between the walls of the tube, the reaction mixture, and the thermometer. Heating and stirring were continued until the entire mass solidified. The time of heating to complete solidification was 15 minutes. Sample V was obtained by heating the polymerized solid in an oven at 550°C for 50 minutes. The elemental analyses of the samples are given in Table I and they are plotted in Figure 1.

b. Identification of volatile products

The method used to trap the volatile compounds evolved when N-trimethylsilylhexaphenylcyclotrisilazane was polymerized was the same used in previous work on hexaphenylcyclotrisilazane.<sup>2</sup>

Approximately 1.8 g of N-trimethylsilylhexaphenylcyclotrisilazane was placed in the reaction vessel and weighed. The apparatus was assembled and swept with dry nitrogen. The nitrogen flow was stopped, the receiver was chilled, and the reaction vessel was heated gently with a burner to start condensation polymerization of the N-trimethylsilylhexaphenylcyclotrisilazane. The volatile material distilled and condensed throughout the system. When solidification became complete in the reaction vessel, heating was stopped. Each section of the apparatus was weighed after it reached room temperature. The starting material lost 0.5546 g or 31% of its weight. The volatile condensation product was analyzed by gas chromatography, and found to be 80% benzene. Ten percent of the products were more volatile than benzene and consisted of four separate compounds including hydrogen and methane. Ten percent were less volatile than benzene. They consisted of 13 compounds and probably included toluene, xylene, and biphenyl, although these were not positively identified.

2. N-Alkyl derivatives of hexaphenylcyclotrisilazane

a. N-Methylhexaphenylcyclotrisilazane

Two reactions were run in attempts to prepare N-methylhexaphenylcyclotrisilazane. The reactions differed in that the first was refluxed at 100°C, while the second was kept below 40°C after the addition of methyl iodide. The crystalline material recovered from each reaction had essentially the same melting-point range, but a higher proportion of the second product was crystalline.

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2. Annual Summary Report, Contract NAS 8-1510, George C. Marshall Space Flight Center, April 29, 1963, pages 72-76 and 161.

The procedure for the second reaction follows: In a 200-ml, 3-neck round-bottom flask fitted with a magnetic stirrer, thermometer, reflux condenser, and dropping funnel were placed 40 ml of purified dioxane and 0.73 g (0.0186 mole, 10% excess) of potassium. The liquid was stirred and heated to 75°C to disperse the potassium. Then 10.0 g (0.0169 mole) of hexaphenylcyclotrisilazane dissolved in 70 ml of dioxane was added. Stirring was continued while the mixture was refluxed for 2.5 hours to allow most of the potassium to react. The solution was cooled to room temperature, and 1.15 ml (2.615 g, 0.0184 mole, 9% excess) of recently distilled methyl iodide dissolved in 10 ml of purified dioxane was added with stirring, over a period of 15 minutes. A white solid formed, giving the solution a cloudy appearance, and the temperature rose 5°C. The mixture was stirred and warmed slightly, but the temperature was kept below 40°C for 3.5 hours. It was then cooled to room temperature and the potassium iodide was filtered off. About 92% of the theoretical amount of potassium iodide was recovered. The dioxane was removed by distillation at reduced pressure, with the temperature of the pot kept below 40°C.

The residue, a soft, tan, partially crystalline material, was dissolved in benzene, and 8.49 g of crystals in several batches having a melting-point range of 149-210°C were recovered by recrystallization from mixtures of benzene and Skellysolve "B". The residue obtained by evaporation of the mother liquor was 1.46 g of a cloudy, yellow, viscous substance.

NMR spectra indicated that the crystalline material was a mixture of mono-, di-, and trimethyl substituents combined with some hexaphenylcyclotrisilazane. Attempts to fractionate these crystals by washing with Skellysolve "B" and recrystallizing from benzene produced no fraction of narrow melting-point range. It was then decided to mix 3.75 g of the lower-melting batches having a melting-point range of 159-197°C and submit these for NMR and infrared analyses and hydrolytic stability and polymerization evaluations.

NMR spectra again indicated three different types of protons in the crystals. This was formerly attributed to the presence of a mixture of mono-, di-, and trimethyl substituents. However, the three types of protons in both samples were in almost equal amounts. Consequently, it seems more likely that each of the three protons was responding individually in the NMR spectrum, and that the di- and tri-substituted materials were not present. The methyl protons were probably being split into a triplet by the nitrogen atom.

The procedure for determining the hydrolytic stability was the same as previously reported.<sup>3</sup> The data are given in Table II and plotted in Figure 2, which are in Section VI. The compound was more stable than hexaphenylcyclotrisilazane, and so it appears that methyl substitution had a stabilizing effect.

b. N-Butylhexaphenylcyclotrisilazane

The attempt to prepare N-butylhexaphenylcyclotrisilazane did not produce a pure compound, but reaction occurred to form a mixture of compounds that probably were N-butyl derivatives.

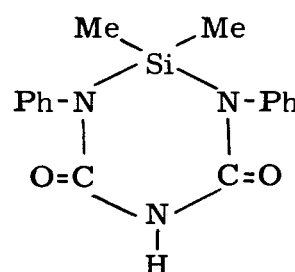
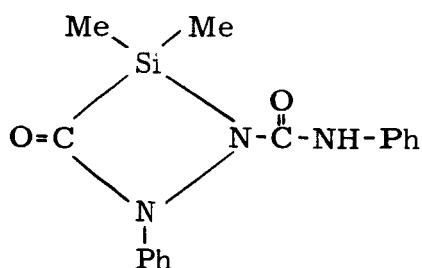
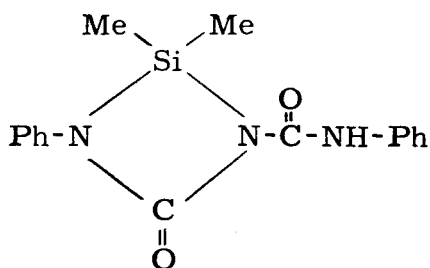
In a 200-ml, 3-neck, round-bottom flask equipped with magnetic stirrer, thermometer, reflux condenser and dropping funnel were placed 40 ml of purified dioxane and 0.73 g (0.0183 mole, 10% excess) of potassium. The mixture was stirred and warmed to 65°C to disperse the potassium. Then 10.0 g (0.0169 mole) of hexaphenylcyclotrisilazane in 70 ml of dioxane was added. Stirring was continued while the mixtures were refluxed for 4 hours, and most of the potassium dissolved. The solution was cooled to room temperature, and 2.10 ml (3.39 g, 0.0184 mole, 9% excess) of 1-iodobutane in 10 ml of purified dioxane was added dropwise with stirring. Heat was added, and the solution began to turn cloudy at 70°C. It was allowed to reflux at 100°C for 2.5 hours. At the end of this time the white solid, potassium iodide, was filtered out. About 65% of the theoretical amount of potassium iodide was recovered. The dioxane was removed by distillation, and the residue was a viscous, yellow, partially crystalline mixture. The mixture was dissolved in 25 ml of benzene, and 3.20 g of crystals, m.p. 195-212°C, were obtained by recrystallization. These were probably hexaphenylcyclotrisilazane. The mother liquor was then evaporated to dryness leaving a sticky resinous product weighing 8.20 g. An attempt was made to distill this at low pressure (0.01-0.02 mm). However, the product evolved a low-boiling material without distilling. Heating was continued for about 5 hours. Samples were withdrawn at 30 minute intervals throughout the process. These samples could be drawn into long, brittle fibers indicating polymerization. The softening points of these samples ranged from 56°C at the beginning of the process to 95°C when the polymerizing operation was terminated. The pot temperature at the end of the process was about 200°C. The temperature was then increased in an attempt to force distillation, but extensive decomposition occurred and a char was obtained.

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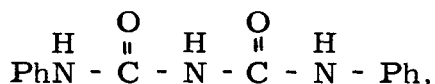
3. Annual Summary Report, Contract NAS 8-1510, George C. Marshall Space Flight Center, April 29, 1963, page 26.

### III. REACTION OF HEXAMETHYLCYCLOTRISILAZANE WITH PHENYL ISOCYANATE

The preceding report described the reaction of hexamethylcyclotrisilazane with phenylisocyanate to produce a compound that probably has one of the three following formulas, all of which agree with the observed data on molecular weight and elemental composition.



Only a small amount of additional work has been done to determine which of the three possible formulas is applicable. Hydrolysis studies have been inconclusive because the hydrolysis product melts at about the same temperature as the starting material. The hydrolysis product could be a compound such as diphenylbiuret,

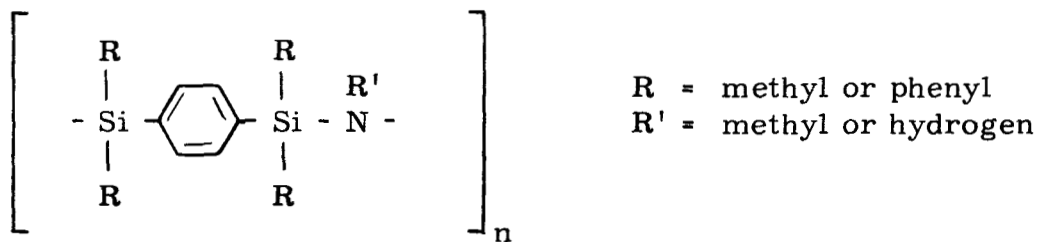


which melts at 210°C. It is worth some effort to identify the compound, because that will show how hexamethylcyclotrisilazane reacted with phenylisocyanate. However, no product has been obtained that appears to be useful, and so only a small amount of additional time will be allotted to trying to identify the hydrolysis product.

#### IV. SILICON-NITROGEN POLYMERS CONTAINING AROMATIC BRIDGES

##### A. Discussion

Work on silicon-nitrogen polymers with phenylene groups in the main chain is being continued. This appears to be a promising route to linear polymers, which are expected to have exceptional stability because of the large amount of aromaticity. In addition, the polymerization reaction is expected to form linear rather than cyclic products because of the shape of the chlorosilane starting materials. The formula of the expected polymers is:



The preceding work was described in Report 30.

Four products were made that may be represented by the formula above. They were white or creamy waxy solids except the one in which both R and R' were methyl. It was a viscous liquid. All four could be polymerized further by heating on a spatula, and during the polymerization, fibers could be drawn from the melts. The films on the spatulas were finally heated to dull redness which caused the polymers to become solid and infusible, but they did not disintegrate. On the basis of this encouraging preliminary examination, the investigation of methods of polymerization of this type of product will be continued.

## B. Experimental Details

### 1. Preparation of 1,4-bis(diphenylchlorosilyl)benzene

The preparation of 1,4-bis(diphenylchlorosilyl)benzene was started in a 5-liter, 3-neck flask fitted with a stirrer and an extraction device. The extraction device consisted of a still with a partial take-off head which condensed the distillate and delivered it to a reservoir of *p*-dibromobenzene. After it trickled through the dibromobenzene, the distillate was returned to the reaction flask. The distilling-extraction cycle ran continuously, and the rate of extraction was controlled by the boil-up rate and partial take-off control.

In the reaction vessel, were placed 62.0 g (2.54 moles) of magnesium turnings, 500 ml of dry diethyl ether, and 643 g (2.54 moles) of diphenyldichlorosilane. The system was swept with dry nitrogen, and the reaction was started by adding 8 g of methyl iodide. The flask was warmed slightly to reflux the ether which extracted the *p*-dibromobenzene (200.0 g, 0.85 mole) from its reservoir. As the dibromobenzene returned to the flask, the exothermic reaction kept the ether distilling. When the extraction was complete the reaction subsided, and the mixture was refluxed for 2 hours. The mixture was filtered inside a polyethylene bag filled with dry nitrogen, the cake was washed with ether, and the ether solutions were combined and distilled. The distillation was interrupted three times to remove the magnesium salts by filtration. When most of the ether was gone, 500 ml of *n*-heptane was added to precipitate the 1,4-bis(diphenylchlorosilyl)benzene. The total product was 24 g of a tan, crystalline material.

The neutral equivalent of the product was 269 (theory, 255.8).



2. Reaction of 1,4-bis(diphenylchlorosilyl)benzene with ammonia

The reaction with ammonia was run as follows: In a 300-ml, 3-neck flask fitted with thermometer, magnetic stirrer, reflux condenser, and gas-inlet tube were placed 200 ml of dry benzene and 12 g (0.023 mole) of 1,4-bis(diphenylchlorosilyl)benzene. The solution was stirred in an atmosphere of ammonia 2 hours and then refluxed for 1 hour. The solution was allowed to stand overnight. The Beilstein Test for halogens in the clear, supernatant liquid was negative, so the solid was filtered off, and the benzene was removed by distillation. The product (9.7 g) was a white waxy solid.

3. Reaction of 1,4-bis(diphenylchlorosilyl)benzene with methylamine

The reaction with methylamine was run as follows: In a 300-ml, 3-neck flask fitted with thermometer, magnetic stirrer, reflux condenser, and gas-inlet tube were placed 12.0 g (0.023 mole) of 1,4-bis(diphenylchlorosilyl)benzene and 200 ml of benzene. Methylamine was passed over the stirred contents of the flask for 2 hours. The reaction mixture was refluxed for 1 hour and allowed to stand overnight. The Beilstein Test for halogens in the supernatant liquid was negative, so the solid was filtered off, and the benzene was removed by distillation. The product, 11.0 g, was a tan, waxy solid.

4. Reaction of 1,4-bis(dimethylchlorosilyl)benzene with methylamine

The reaction of 1,4-bis(dimethylchlorosilyl)benzene (Report 30) was run as follows: In a 300-ml, 3-neck flask fitted with a thermometer, stirrer, reflux condenser, and gas-inlet tube were placed 18.6 g (0.071 mole) of 1,4-bis(dimethylchlorosilyl)benzene and 225 ml of dry benzene. The solution was stirred in an atmosphere of methylamine for 2 hours, and then refluxed for 1 hour. The Beilstein Test for halogens was negative. The solid was filtered off, and the benzene was distilled. The yellow, viscous, liquid product weighed 15.3 g.

## V. REACTION OF METHYLPHENYLDICHLOROSILANE WITH AMMONIA AND METHYLAMINE

### A. Discussion

In the search for methods of making polymers for structural plastics from silicon-nitrogen compounds, the polymerization of methylphenyl silazanes is being studied. Previously,<sup>4</sup> the methylphenyl silazanes were judged to polymerize to coatings that were more flexible than those obtained from hexaphenylcyclotrisilazane. Accordingly, the study of them is being resumed; and, in addition, N-methyl derivatives will be included to modify the functionality of the nitrogen groups.

When methylphenyldichlorosilane was treated alternately with methylamine and ammonia, the product contained N-methyl and N-hydrogen groups in a 15:100 ratio. Evaluation of the material in coatings revealed no outstanding properties in regard to flexibility or thermal stability. When methylphenyldichlorosilane was treated with a mixture of methylamine and ammonia, the methylamine did not react. Attempts to polymerize the material with N-methyl groups will be continued.

### B. Experimental Details

#### 1. Reaction of methylphenyldichlorosilane with a mixture of ammonia and methylamine

In a 500-ml, 3-neck flask fitted with stirrer, reflux condenser, thermometer, and gas-inlet tube were placed 200 ml of dry benzene and 30 g (0.157 mole) of methylphenyldichlorosilane. Three moles of methylamine and 3 moles of ammonia were mixed in a flask and dried over sodium. The mixed vapors were allowed to distill and were passed over the stirred solution for 2.5 hours. At the end of this time, the clear supernatant liquid was negative to the Beilstein Test for halogens. The solution was refluxed for 2 hours, cooled, and filtered. The benzene was distilled off leaving 19 g of cloudy, colorless liquid. NMR spectra showed that no N-methyl groups were present.

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4. Annual Summary Report, Contract DA-01-009-ORD-829, U. S. Army Ballistic Missile Agency, February 20, 1961, pages 30 and 44.

The liquid product was spread on aluminum and heated at 450°C for 30 minutes. The coating remained intact even after the panel was bent and placed in 1:1 hydrochloric acid until the uncoated areas were badly etched. Heating at 450°C for longer periods caused the coating to crack on being bent.

## 2. Reaction of methylphenyldichlorosilane alternately with methylamine and ammonia

To obtain partial reaction of methylphenyldichlorosilane with methylamine it was necessary to alternate the addition of methylamine and ammonia. In a 500-ml, 3-neck flask fitted with stirrer, reflux condenser, and two gas-inlet tubes were placed 250 ml of dry benzene, and 30.0 g (0.157 mole) of methylphenyldichlorosilane. From two separate flasks, ammonia and methylamine were passed over the reaction at the same time for 15 minutes. Then methylamine was passed in for 15 minutes followed by ammonia for 10 minutes. The alternation was repeated twice more making a total amination time of 1.5 hours. The solution was refluxed for 2 hours, and then the clear supernatant benzene layer was negative to the Beilstein Test for halogens. The precipitate was filtered off, and the benzene was distilled. The product was 18.5 g of a slightly viscous, yellow liquid. The NMR spectrum showed the ratio of N-methyl groups to N-hydrogen groups to be 15:100.

About 4 g of the product was placed in a distilling flask, and half of it was distilled at 378-394°C by heating with a gas flame. Then heavy smoking began, and the efforts to distill were discontinued. The undistilled portion undoubtedly had been much hotter than 394°C, but the actual temperature was not determined. It was largely a foamed brittle solid.

Almost the entire product was distilled at 191-203°C at 0.1 mm. The distillate was a cloudy, colorless, viscous liquid, which crystallized partially on standing. This reaction could probably be used to produce a material that would be fluid over the range of 20-400°C, if there is a need for such a liquid.

## VI. COMPARISON OF HYDROLYTIC STABILITIES

The hydrolytic stabilities of silicon-nitrogen compounds have been compared by measuring the rate of formation of titratable base when the compound dissolved in benzene or carbon tetrachloride was shaken with water or water and hydrochloric acid. Previous results were discussed in the preceding annual report,<sup>5</sup> and the preceding quarterly summary (Report 29). The compound compared in the past month was the N-methyl derivative of hexaphenylcyclotrisilazane that was not fully purified and characterized (Section II). The results of its hydrolysis in benzene-water-hydrochloric acid are in Table II with comparable results obtained with hexaphenylcyclotrisilazane. The data are plotted in Figure 2. It is evident that the compound is more stable than hexaphenylcyclotrisilazane.

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5. Annual Summary Report, Contract NAS 8-1510, George C. Marshall Space Flight Center, April 29, 1963, Section IV.

Table II. Relative Rates of Hydrolysis of Silylamines

	$C_6H_5 + H_2O$		$C_6H_5 + H_2O + HCl$	
	min	%	min	%
Mixed N-methylhexaphenyl- cyclotrisilazane				
Compound 3273-105-1	-	0.9	98	14
Hexaphenylcyclotrisilazane			5	42

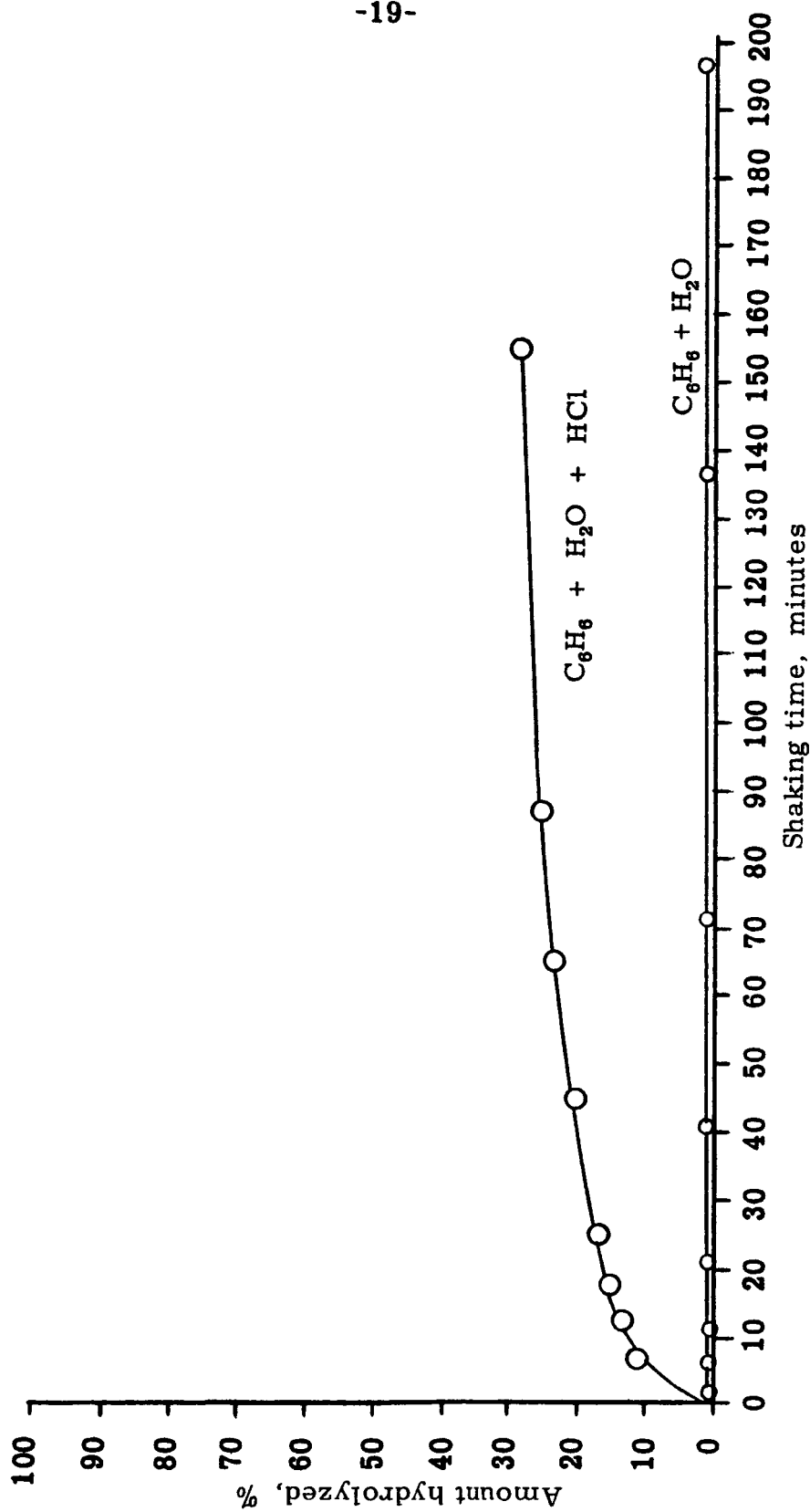


Figure 2. Hydrolysis of N-Methyl Derivative of Hexaphenylcyclotrisilazane.

## VII. POLYMERIZATION OF HEXAPHENYLCYCLOTRISILAZANE IN SEALED VESSELS AT HIGH TEMPERATURE

Groszos and Hall<sup>6</sup> stated that hexaphenylcyclotrisilazane could be polymerized in sealed vessels at temperatures up to 700°C to produce thermoplastic polymers. If their polymerization produced a different type of polymer from the prepolymer made by heating at atmospheric pressure, it would be worth some trials in coatings and heat barriers. However, if their polymer is the same as ours, there would be no advantage in using their method. Our infusible polymer is different from theirs.

Hexaphenylcyclotrisilazane, 1.97 g was placed in a 45-ml, stainless-steel bomb and heated at 600°C for 10 minutes. The bomb was cooled and opened, and the product was found to be a brown, brittle solid. It was soluble in benzene and had a melting range of 173-202°C. Evidently this was a satisfactory example of their product. It was suspected of being very much like the prepolymer that we have often made from hexaphenylcyclotrisilazane, because it performed almost identically when made into coatings on aluminum in that it was stable but brittle. Consequently, to check the similarity further, a prepolymer was made by our method by boiling hexaphenylcyclotrisilazane in a test tube at atmospheric pressure until it appeared to be about to solidify. After being cooled, pulverized, and placed in a capillary tube, it melted at 195-216°C.

Intrinsic viscosities of both products showed that they both had low molecular weights, that of the prepolymer being slightly higher. In previous work,<sup>7</sup> the highest molecular weight determined for a prepolymer was 1400. There seems to be no advantage in studying the Groszos and Hall method further.

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6. S. J. Groszos and J. A. Hall, U. S. Patent 2,885,370 (to American Cyanamid Company), May 5, 1959.
  7. Annual Summary Report, Contract NAS 8-1510, George C. Marshall Space Flight Center, April 29, 1963, page 72.

### VIII. ANTICIPATED WORK

Efforts to attach alkyl side chains to silazanes will be continued. We will emphasize long alkyl side chains to increase the probability of obtaining liquid products that may be useful as lubricants or hydraulic fluids.

In the coming month, we will attempt to conclude the work on thermal methods of polymerizing methylphenyl silazanes with end-amino groups. We will attempt to reach a conclusion, also, on polymer formation by treating alkali derivatives of silazanes with dichlorosilanes.

Work will be continued on silicon-nitrogen polymers with phenylene bridges. Apparently, we now have compounds with phenylene bridges and end-amino groups, and we want to polymerize them by heating.

### IX. TIME EXPENDITURE

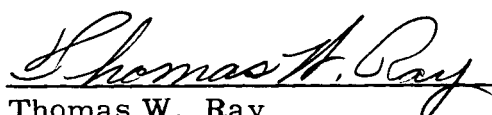
The time expenditure during the monthly period covered by this report was 863.5 man-hours.

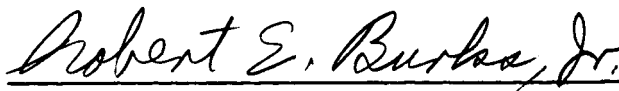


ACKNOWLEDGMENTS


Mr. Robert E. Lacey, Senior Chemical Engineer, has assisted with the planning and interpretation of the laboratory work. Miss Mary Ann Fromhold, Assistant Chemist; Mr. Charles L. Christy, Jr., Chemical Technician; and Mr. Jerald T. LeBlanc, Laboratory Helper, assisted with the laboratory work.

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# PROGRAM PLANNING CHART

	Allotted time, man-hours	1983												1984		
		April	May	June	July	August	September	October	November	December	January	February	March			
A. Synthesis of Polymers and Compounds with Desired Characteristics																
1. Lubricants - unsymmetrical derivatives of cyclic silazanes (see B. 1. b)	400			X	X	X										
2. Elastomers - silyl derivatives of ethylenediamine (see B. 7)	400															
3. Structural plastics	900	X	X	X	X	X										
B. Study of the Chemistry of Silicon-Nitrogen Compounds																
1. Metalation of silylamines as a method of synthesis	500	X	X	X	X	X										
a. Polymers	-															
b. Lubricants (see A. 1)	900							X	X	X	X	X	X			
c. Organometallics																
2. Polymerization of cyclic silazanes at high temperatures and pressures	280			X	X											
3. Condensation polymerization of silylamines with difunctional aromatic compounds	280															
4. Steric factors to inhibit cyclization	900							X	X	X	X	X	X			
5. Polyethylenimine as a source of silicon-nitrogen polymers	400							X	X	X	X	X	X			
6. Properties of methylhydrogen silazanes	200							X	X	X	X	X	X			
7. Elastomers from ethylenediamine silazanes (see A. 2)	-															
8. Addition of silicon tetrafluoride to silazanes and amines	280															
9. Heats of combustion as indicators of aromaticity	420															
10. Polymers from methyltrichlorosilane and silicon tetrachloride	420															
11. Silicon-nitrogen compounds with aromatic bridges	510	X	X	X	X	X		X	X	X	X	X	X			
12. Factors affecting hydrolytic and thermal stabilities	510			continuous												
C. Evaluation of Polymers (thermal, hydrolytic, and radiation stability)	510															
D. Applications - Search for New Uses	510															
E. Heat Barriers	510															
F. Preparation of Final Report	170															
	9000															X

Descriptions correspond to sections of Proposal 2186 - March 20, 1983.